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Palladium incorporated on carbonaceous catalyst for Suzuki coupling reaction in water

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ABSTRACT

A new palladium incorporated carbonaceous catalyst Pd@CC—SO_3H—NH_2 was synthesized by introducing palladium on glucose derived carbocatalyst. The catalyst was well characterized and was used for the Suzuki coupling of phenyl boronic acid with different aryl halides under aqueous conditions. This green methodology represents a ligand free, cost-effective and operationally convenient method for the synthesis of a variety of biaryl's under the conditions that are tolerant for a broad range of functional groups with good to excellent yields. Moreover, the catalyst could be easily recycled and reused at least five times without any significant loss of its catalytic activity.

Palladium (Pd) chemistry has emerged as one of the most powerful tool for formation of carbon-carbon bond. Suzuki coupling is a powerful tool for constructing structures for biaryl's that exists in many biologically active compounds and natural products.[1] Usually, Suzuki coupling is catalyzed by palladium complex under homogeneous conditions.[2–5] But several disadvantages of homogenous catalyst such as high cost, difficulty in separation limits its use on an industrial scale. Thus, developing palladium containing heterogeneous catalyst for Suzuki coupling has gained lot of attention.[6–15] Recently, carbonaceous catalysts have also gained significant importance as an attractive heterogeneous catalyst.[16,17] According to the green chemistry principles, biomass-derived carbonaceous catalysts are environmentally benign and highly economical as compared to the other existing heterogeneous catalysts for organic transformations. Due to the hydrophobic and chemically inert nature of the carbon materials, low cost, easy accessibility, good recycling characteristics, surface hydrophobicity, low density, and most importantly the possibility to introduce different functionalities through a wide range of activation, functionalization and carbonization methods they are more advantageous in different aqueous phase reactions. Carbonaceous materials are more resistant to structural changes by hydrolytic effects in aqueous environments as compared to silica or alumina supports. Intrigued by these studies and our continuing work in this field,[18] we choose readily available glucose as a carbon precursor which is the main component of biomass for the synthesis of Pd@CC—SO_3H—NH_2 catalyst. In this work, we discuss the synthesis of Pd@CC—SO_3H—NH_2 catalyst and tested its activity in Suzuki coupling reaction.

For the preparation of Pd@CC—SO_3H—NH_2 catalyst, we choose readily available D-glucose as a carbon precursor. The first step was hydrothermal carbonization of glucose and *p*-TSA. The hydrothermal carbonization promoted the structure to undergo decomposition, hydrolysis, dehydration, and molecular rearrangement reaction to produce a polycyclic aromatic structure embedded with active —SO_3H, —COOH and —OH sites.[19] In the second step, 3-amino propyl triethoxy silane in ethanol was added to generate the basic —OSi—$CH_2CH_2CH_2NH_2$ site on the catalyst followed by incorporation of palladium on the catalyst surface using $PdCl_2$ in methanol. The Pd@CC—SO_3H—NH_2 catalyst thus obtained was characterized with FT-IR (Spectrum 400), Elemental analysis from EDAX (Nova Nano SEM 450), XPS (Multilab, V G Mircrotech, ESCA 3000), SEM (Quanta™ Scanning Electron Microscope) and TEM (Tecnai 4220 S-Twin). The FT-IR spectrum (Fig. S1, Supp inf.) showed characteristic peaks at 1018 cm^{-1} and 1033 cm^{-1} which are attributed to O=S=O stretching vibrations in —SO_3H groups and peak at 1152 cm^{-1} for SO_3— stretching, indicating the presence of sulfonic acid groups on the catalyst surface. Peaks at 1658 cm^{-1} and 1696 cm^{-1} attributed to the C=C stretching vibrations in aromatic carbons and C=O stretching, respectively. Peak at 1701 cm^{-1} corresponds to the presence of C=O stretching vibration of —COOH group. Doublet at 2923 cm^{-1} attributed for C—H stretching band

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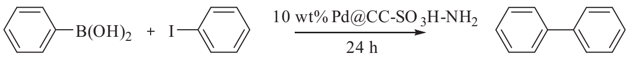
and a peak at 1453 cm^{-1} indicated C—H bending vibration of alkyl groups of amine terminal silanes. Stretching vibrations for Si—O at 1057 cm^{-1} and stretching and bending vibrations of Si—O—C at 1114 cm^{-1} and 681 cm^{-1} indicated that silylanization occurred on the catalyst surface. The peak at 1591 cm^{-1} due to the N—H bending vibrations confirmed the presence of amino group on the surface of the catalyst. Bands due to O—H stretching were observed at 3429 cm^{-1}. Energy dispersive X-ray analysis (EDAX) (Fig. S2, Supp inf.) showed the presence of nitrogen, sulphur, silicon, palladium and chloride thus confirming the acidic —SO_3H, basic *O*Si—$CH_2CH_2CH_2NH_2$ and coordination of palladium to the NH groups on the surface of the Pd@CC—SO_3H—NH_2 catalyst. These results were further confirmed by XPS analysis (Fig. S3, Supp inf.). In N1s, XPS peak at 389 eV attributed to the stronger coordination bond between ethylene diamine group and Pd centers. Pd species in Pd@CC—SO_3H—NH_2 corresponded to binding energy of 352 eV. Peak at 583 eV was observed for O1s. SEM analysis (Fig. S4, Supp inf.) showed a typical planar structure of Pd@CC—SO_3H—NH_2 carbonaceous catalyst maintaining two dimensional structures with heavy crumpling features. TEM analysis (Fig. S5, Supp inf.) showed aggregates of particular morphology of Pd@CC—SO_3H—NH_2 carbonaceous catalyst.

The performance of Pd@CC—SO_3H—NH_2 catalyst was tested for the Suzuki coupling reaction. Phenyl boronic acid and iodobenzene were selected as a model substrate for the Suzuki reaction. As shown in Table 1, the catalytic activity of Pd@CC—SO_3H—NH_2 catalyst was studied in different solvents initially in the absence of base for 24 h. It was found that ethanol and DMSO gave about 56 and 37% yield of the biphenyl (Table 1, entries 1 & 2) whereas isopropanol, toluene, water, sulpholane, water: ethanol gave less than 35% yield of the biphenyl (Table 1, entries 4, 5, 7, 8 & 9). Tetrahydrofuran, *N*-methylpyrrolidone, methylacetate and solvent free condition's showed no formation of biphenyl (Table 1, entries 3, 10, 11, & 12). It was found that the catalyst was most effective in solvent DMF giving 89% yield of the biphenyl at 140 °C (Table 1, entry 6).

We then attempted the Suzuki reaction of phenyl boronic acid and iodobenzene using K_2CO_3 as a base and screened the solvents for Suzuki coupling. As shown in Table 2, similar set of experiments were repeated as in Table 1, in the presence of K_2CO_3 as a base. It was observed that when Suzuki coupling was carried out using

Table 1
Optimization of Suzuki coupling reaction in different solvents.[a]



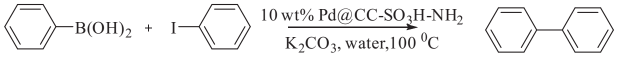
Entry	Solvent	Temp (°C)	Yield (%)[b]
1	EtOH	70	56
2	DMSO	140	37
3	THF	60	–
4	IPA	70	24
5	Toluene	100	29
6	DMF	140	89
7	Water	100	21
8	Sulpholane	140	34
9	H_2O:EtOH	70	24
10	N-methylpyrrolidone	140	–
11	Methyl acetate	50	–
12	Neat	100	–

Reaction conditions:

[a] Phenylboronic acid (1 mmol), iodobenzene (1 mmol), Pd@CC—SO_3H—NH_2 catalyst (10 wt%).

[b] Isolated yield.

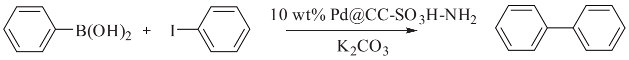
Table 3
Optimization of Suzuki coupling reaction varying base concentration.



Entry	K_2CO_3 (mmol)	Time (h)	Yield (%)[a]
1	1	9	96
2	2	6.5	95
3	3	5	96
4	4	4.5	95
5	5	3.5	95
6	6	2	96
7	7	2	96

[a] Isolated yield.

Table 2
Optimization of Suzuki coupling reaction in different solvents using K_2CO_3 as a base.[a]



Entry	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	EtOH	70	6	89
2	DMSO	140	8	51
3	THF	60	24	–
4	IPA	70	3.5	48
5	Toluene	100	24	55
6	DMF	140	9.5	93
7	Water	100	2	96
8	Sulpholane	140	24	35
9	H_2O:EtOH	70	3.5	80
10	N-methylpyrrolidone	140	24	–
11	Neat	100	24	–
12	Methyl acetate	50	24	24
13[c]	Water	100	24	–
14[d]	Water	100	24	–

Reaction conditions:

[a] Phenylboronic acid (1 mmol), iodobenzene (1 mmol), Pd@CC—SO_3H—NH_2 catalyst (10 wt%), K_2CO_3 (6 mmol).

[b] Isolated yield.

[c] Reaction carried out using CC—SO_3H—NH_2 catalyst.

[d] Reaction carried out in absence of catalyst.